

CONCERNING A FILING UNDER 35 U.S.C. 371

09/462109

INTERNATIONAL APPLICATION NO.

PCT/JP98/02954

INTERNATIONAL FILING DATE

29, June, 1998 (29.06.98)

PRIORITY DATE CLAIMED

2, July, 1997 (02.07.97)

TITLE OF INVENTION

Composite Reverse Osmosis Membrane and Method of Producing the Same

APPLICANT(S) FOR DO/EO/US

HIROSE, Masahiko; ITO, Hiroki; and OHARA, Tomomi

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an **express** request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Request for PCT Application and English Translation of same

A copy of published WO99/01208

A copy of the English translation of the Written Amendment under Article 34

A copy of the English translation of the Written Reply under Article 34

Notice Informing the Applicant of the Communication of the International Application to the Designated Offices

Acknowledgement postcard

English Translation of PCT Chapter II Demand

20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Search Report has been prepared by the EPO or JPO \$840.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00
- ☒ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$960.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). ☐ 20 ☐ 30

\$970.00

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	17 - 20 =	0	x \$18.00	\$0.00
Independent claims	2 - 3 =	0	x \$78.00	\$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00

TOTAL OF ABOVE CALCULATIONS = \$970.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00

SUBTOTAL = \$970.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐ 20 ☐ 30

\$0.00

TOTAL NATIONAL FEE = \$970.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☒

\$40.00

TOTAL FEES ENCLOSED = \$1,010.00

Amount to be:
refunded \$
charged \$

☒ A check in the amount of \$1,010.00 to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **50-0591** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Jonathan P. Osha, Reg. No. 33,986

ROSENTHAL & OSHA L.L.P.
700 Louisiana Street, Suite 4550
Houston, Texas 77002

Telephone: (713) 228-8600
Facsimile: (713) 228-8778

SIGNATURE

Jonathan P. Osha

NAME

33,986

REGISTRATION NUMBER

December 30, 1999

DATE

DESCRIPTION

COMPOSITE REVERSE OSMOSIS MEMBRANE AND METHOD OF PRODUCING THE SAME

5

TECHNICAL FIELD

The present invention relates to a composite reverse osmosis membrane for selectively separating components in a liquid mixture, and a method of producing the membrane. More specifically, the present invention relates to a composite reverse osmosis membrane having a porous support on which a polyamide skin layer mainly comprising polyamide is formed to provide both high salt rejection and high permeability, and a method of producing the same.

Such a composite reverse osmosis membrane can be used for many purposes, including the manufacture of ultra-pure water and the desalination of sea water or brackish water. This membrane also can be used to remove contamination from a source or withdraw purified materials from contaminated dyeing waste or electrochemical deposition coating waste. Such wastes may cause pollution. Thus the present invention will clean contaminated water to be reused. The membrane of the present invention also can be used for other purposes like condensing effective components for food.

BACKGROUND ART

Conventionally, composite reverse osmosis membranes have been known as reverse osmosis membranes which differ in structure from asymmetric reverse osmosis membranes. Such composite reverse osmosis membranes are produced by forming active thin films (skin layers) which possess the ability to selectively separate materials, on porous supports.

Applications disclose membranes comprising polyamide obtainable by interfacial polymerization between polyfunctional aromatic amines and polyfunctional aromatic acid halide compounds formed on porous supports. The examples of such applications are, JP-A-(Unexamined Published Japanese Patent Application) 55-147106, JP-A-62-121603, JP-A-63-218208, and JP-A-2-187135. Other prior art references disclose composite reverse osmosis membranes wherein skin layers comprising polyamide are formed on porous supports, and the polyamide is obtained by an interfacial

polymerization of a polyfunctional aromatic amine and a polyfunctional alicyclic acid halide compound (cf. JP-A-61-42308).

The composite reverse osmosis membranes described above have a high desalination property and a high water permeability, but it is desirable to improve the water permeability while keeping the high desalination property from the standpoint of the efficiency and so on. For these requirements, various kinds of additives are proposed e.g., in JP-A-63-12310. However, in the conventional composite reverse osmosis membranes, the improvement of the properties of the composite reverse osmosis membranes are still insufficient.

JP-A-63-178805 discloses a method of forming a membrane in a two-stage reaction. In this method, a polyfunctional reaction reagent of a low concentration is added in the second stage. A composite reverse osmosis membrane obtained in this method is improved slightly in the salt rejection, but the permeation speed is lowered instead. This method cannot provide a composite reverse osmosis membrane to conform to the requirements.

The present invention aims to provide a composite reverse osmosis membrane having a high salt rejection and high water permeability, and a method of producing the same.

DISCLOSURE OF THE INVENTION

In order to accomplish these objects, a composite reverse osmosis membrane of the present invention comprises a polyamide skin layer formed on a porous support, and the contact angle between the polyamide skin layer surface and water is defined not to exceed 45°.

When the contact angle is no more than 45°, a high salt rejection is maintained, a flux is improved and thus, the membrane has excellent water permeability. The contact angle is preferably 40° or less.

In the present invention, the contact angle is measured in the following manner. First, the polyamide skin layer surface is cleansed and dried. Then, pure water is dropped on the surface in order to measure the angle (the internal angle of the water drop) formed by the water drop and the polyamide skin layer. The angle is measured preferably about 15 seconds after the dropping of the water.

The composite reverse osmosis membrane preferably includes a polyamide skin layer formed by a reaction of one or more compounds having at least two reactive amino groups and one or more polyfunctional acid halide

compounds having at least two reactive acid halide groups.

Preferably, the composite reverse osmosis membrane provides a salt rejection of at least 98% and a permeate flow rate of at least $0.5\text{m}^3/\text{m}^2\cdot\text{day}$ when evaluated by using feed water having pH 6.5 containing 0.05 weight % of salt at an operation pressure of $5\text{kgf}/\text{cm}^2$ and a temperature of 25°C . If the salt rejection and the permeate flow rate are within these ranges, ions can be removed if an actual operation pressure is low as $5\text{kgf}/\text{cm}^2$ or less, for example, about $3\text{kgf}/\text{cm}^2$. Therefore, facilities comprising the composite reverse osmosis membranes can be built by using pipes made of inexpensive materials such as polyvinyl chloride. This offers a significant cost advantage. The composite reverse osmosis membrane can be used at city water level pressures. Preferably, the salt rejection is at least 98%, the permeate flow rate is at least $0.6\text{m}^3/\text{m}^2\cdot\text{day}$ under the above-identified condition. Most preferable is if the salt rejection is at least 99% and the permeate flow rate is at least $0.7\text{m}^3/\text{m}^2\cdot\text{day}$.

A method of producing a composite reverse osmosis membrane of the present invention includes the steps of:

forming a layer by coating on a porous support a solution A comprising one or more compounds having at least two reactive amino groups; contacting this layer with a solution B comprising one or more polyfunctional acid halide compounds; and

further contacting the layer with another solution C comprising one or more polyfunctional acid halide compounds of a concentration higher than the solution B in order to form a polyamide skin layer on the porous support.

The above-identified composite reverse osmosis membrane can be produced in this method.

The composite reverse osmosis membrane of the present invention is preferably produced in this method, but it is not limited thereto.

In the producing method, preferably, the concentration of the polyfunctional acid halide compound in the solution C is at least 1.2 times of the polyfunctional acid halide compound in the solution B. More specifically, the difference in the concentration ranges from 1.3 times to 5000 times. When the concentration of the solution C is less than 1.2 times of the solution B, the obtained composite reverse osmosis membrane may not have a high salt rejection or a high permeate flow rate. On the other hand, when the concentration of the solution C exceeds 5000 times of the solution B, the

properties cannot be improved to match with the difference, and it causes disadvantages in costs and efficiency. The standard of the concentration is not specifically limited, but it can be, for example, based on weight.

5 Preferably in the producing method, solution B remains partially unreacted at a contact with the solution C.

The remaining solution B can be observed visually after a contact with the solution C. A composite reverse osmosis membrane having a high salt rejection and a high permeate flow rate can be obtained even if the solution B does not remain. However, the properties of the composite reverse osmosis membrane can be improved if some solution B remains.

10 In the present invention, the compound included in the solution A preferably has at least two amino groups and the compound is at least one selected from the group consisting of aromatic polyfunctional amine, aliphatic polyfunctional amine and alicyclic polyfunctional amine.

15 A preferable aromatic polyfunctional amine is selected from the group consisting of m-phenylenediamine, p-phenylenediamine, 1,3,5-triaminobenzene, 1,2,4-triaminobenzene, 3,5-diamino benzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, amidol, and xylenediamine. These amines can be used either alone or as mixtures thereof.

20 A preferable aliphatic polyfunctional amine is selected from the group consisting of ethylenediamine, propylenediamine, and tris(2-aminoethyl)amine. These amines can be used either alone or as mixtures thereof.

25 A preferable alicyclic polyfunctional amine is selected from the group consisting of 1,3-diaminocyclohexane, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, piperazine, 2,5-dimethylpiperazine, and 4-aminomethylpiperazine. These amines can be used either alone or as mixtures thereof.

30 The polyfunctional halide compound included in the solution B or C is preferably at least one selected from the group consisting of aromatic polyfunctional acid halide compound, aliphatic polyfunctional acid halide compound and alicyclic polyfunctional acid halide compound.

35 Preferably, the aromatic polyfunctional acid halide compound is selected from the group consisting of trimesic acid chloride, terephthalic acid chloride, isophthalic acid chloride, biphenyldicarboxylic acid chloride, naphthalenedicarboxylic acid dichloride, benzene trisulfonic acid chloride, benzene disulfonic acid chloride, and chlorosulfonium benzene dicarboxylic

acid chloride. These compounds can be used either alone or as mixtures thereof.

Preferably, the aliphatic polyfunctional acid halide compound is selected from the group consisting of propanetricarboxylic acid chloride, butanetricarboxylic acid chloride, pentanetricarboxylic acid chloride, glutaryl
5 halide, and adipoyl halide. These compounds can be used either alone or as mixtures thereof.

Preferably, the alicyclic polyfunctional acid halide compound is selected from the group consisting of cyclopropanetricarboxylic acid chloride, cyclobutanetetracarboxylic acid chloride, cyclopentanetricarboxylic acid
10 chloride, cyclopentanetetracarboxylic acid chloride, cyclohexanetricarboxylic acid chloride, tetrahydrofurantricarboxylic acid chloride, cyclopentanedicarboxylic acid chloride, cyclobutanedicarboxylic acid chloride, cyclohexanedicarboxylic acid chloride, and tetrahydrofurantricarboxylic acid
15 chloride. These compounds can be used either alone or as mixtures thereof.

Preferably in the present invention, a polyfunctional acid halide compound included in at least either the solution B or C has a hydrophilic group. The hydrophilic group is preferably at least one selected from the group consisting of $-\text{COOX}$, $-\text{OH}$, $-\text{SO}_3\text{X}$, $-\text{OSO}_3\text{X}$, $-\text{NH}_2$, $-\text{NR}_2\text{Y}$ and
20 $-(\text{OCH}_2\text{CH}_2)-$. 'X' indicates a hydrogen atom, an alkaline metal or $-\text{NH}_4$. 'R' indicates a hydrogen atom or an alkyl group, and 'Y' indicates a halogen. Specific examples of these hydrophilic groups include a carboxyl group, a hydroxyl group, a sulfonic group, and an amino group. Among them, a carboxyl group, a sulfonic group, and an amino group are preferred.

Preferably in the method of the invention, the porous support provided with the layer is further contacted with at least either an acidic aqueous solution or an alkaline aqueous solution after the contact with the solution C. The acidic aqueous solution preferably has a pH ranging from 1 to 5 and it contains acidic materials such as phosphoric acid, hydrochloric acid,
30 sulfuric acid and nitric acid. The alkaline aqueous solution has a pH ranging from 8 to 13, and it contains alkaline materials such as sodium hydroxide.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be further explained below.

35 A compound included in the solution A has at least two reactive amino groups. This compound is not specifically limited but any of the above-mentioned compounds can be used. The solution A is typically an aqueous

solution.

The solution A can contain an ingredient(s) besides the amine ingredient. For example, to facilitate formation of a membrane or to improve the properties of the obtained composite reverse osmosis membrane, small amounts of polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and polyacrylic acid, or small amounts of polyhydric alcohols such as sorbitol and glycerol, can be added.

The solution A preferably includes salts, such as amine salts disclosed in JP-A-2-187135. Most preferable are salts comprising organic acids and tetraalkyl ammonium halide or trialkyl amine. These amine salts improve the absorptivity of the solution A in the support and help promote the reaction by facilitating formation of the membrane.

The solution A can contain a surfactant(s) such as sodium dodecylbenzenesulfonate, sodium dodecyl sulfate, and sodium lauryl sulfate. These surfactants are effective in improving the absorption of the solution A onto the porous support.

In the present invention, the material disclosed in JP-A-8-224452, whose solubility parameter ranges from 8 to 14 (cal/cm³)^{1/2}, can be included in the solution A or in the reactants of the solutions A, B and C, so that the flux will be further improved.

The solubility parameter is the amount defined by $(\Delta H/V)^{1/2}$ (cal/cm³)^{1/2} when the molar heat of vaporization of a liquid is ΔH cal/mol, and the molar volume is V cm³/mol.

Materials having the above solubility parameter include, for example, alcohols, ethers, ketones, esters, halogenated hydrocarbons, and sulfur-containing compounds.

The alcohols include, for example, ethanol, propanol, butanol, butyl alcohol, 1-pentanol, 2-pentanol, t-amyl alcohol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, undecanol, 2-ethyl butanol, 2-ethyl hexanol, octanol, cyclohexanol, tetrahydro furfuryl alcohol, neopentyl glycol, t-butanol, benzyl alcohol, 4-methyl-2-pentanol, 3-methyl-2-butanol, pentyl alcohol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol.

The ethers include, for example, anisole, ethyl isoamyl ether, ethyl-t-butyl ether, ethylbenzyl ether, crown ether, cresyl methyl ether, diisoamyl ether, diisopropyl ether, diethyl ether, dioxane, diglycidyl ether, cineol, diphenyl ether, dibutyl ether, dipropyl ether, dibenzyl ether, dimethyl ether, tetrahydropyran, tetrahydrofuran, trioxane, dichloroethyl ether, butyl phenyl

ether, furan, methyl-t-butyl ether, monodichlorodiethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, and diethylene chlorohydrin.

5 The ketones include, for example, ethyl butyl ketone, diacetone alcohol, diisobutyl ketone, cyclohexanone, 2-heptanone, methyl isobutyl ketone, methyl ethyl ketone, and methyl cyclohexane.

10 The esters include, for example, methyl formate, ethyl formate, propyl formate, butyl formate, isobutyl formate, isoamyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, and amyl acetate.

15 The halogenated hydrocarbons include, for example, allyl chloride, amyl chloride, dichloromethane, and dichloroethane.

The sulfur-containing compounds include, for example, dimethyl sulfoxide, sulfolane, and thiolane.

Among these compounds, alcohols and ethers are especially preferable. These compounds can be used either alone or as mixtures thereof.

20 Furthermore, for accelerating the polycondensation reaction at the interface, it is effective to use sodium hydroxide or sodium tertiary phosphate in the solution A, which is capable of removing a hydrogen halide formed during the interfacial reaction or to use an acylation catalyst.

25 Examples of solvents that are preferably used in the solutions B and C include organic solvents immiscible with water. Among the solvents, for example, hydrocarbons (e.g., hexane, heptane, octane, nonane, decane, and cyclohexane) and halogenated hydrocarbons (e.g., carbon tetrachloride, trichlorotrifluoroethane, and difluorotetrachloroethane) are especially preferred.

30 Polyfunctional acid halide compounds included in the solutions B and C are not specifically limited to the above-identified compounds.

In the present invention, the compound having at least two amino groups and the polyfunctional acid halide compound are interfacially polymerized to form a thin film mainly comprising polyamide (i.e., a polyamide skin layer) on a porous support.

35 For the solutions A, B and C, concentrations of the compound having at least two amino groups and of the polyfunctional acid halide compound are

not specifically limited as long as the concentration ratio of the polyfunctional acid halide in the solution B to that in the solution C is in the predetermined range. Typical concentration of the polyfunctional acid halide compound in the solution B ranges from 0.01 to 5 weight %, or preferably, from 0.05 to 1 weight %. Typical concentration of the polyfunctional acid halide compound in the solution C ranges from 0.02 to 50 weight %, or preferably, from 0.06 to 20 weight %. Typical concentration of the compound having at least two amino groups ranges from 0.1 to 10 weight %, or preferably, from 0.5 to 5 weight %.

The porous support in the present invention is not specifically limited as long as it can support the polyamide skin layer. The support can be made of various materials, for example, polysulfone, polyarylethersulfone such as polyethersulfone, polyimide, and polyvinylidene fluoride. Among them, a porous support film made of polysulfone or polyarylethersulfone is especially preferred because of the chemical, mechanical and thermal stability.

The porous support film is typically about 25-125 μ m thick, preferably about 40-75 μ m thick, but the thickness is not limited thereto.

A composite reverse osmosis membrane of the present invention is produced from the above-identified materials in the following manner. First, the solution A comprising one or more compounds having at least two amino groups is coated on the porous support so as to form a first layer. On the first layer, the solution B comprising one or more polyfunctional acid halide compounds is coated and subsequently, the solution C is coated thereon. The coated support is heated and dried at about 20 to 150°C in general, preferably at about 70 to 130°C for about 1 to 10 minutes, preferably for about 2 to 8 minutes, and thus, a polyamide-based water-permeable thin film (polyamide skin layer) is formed. This thin film is typically about 0.02 to 2 μ m in thickness, preferably about 0.1 to 1.0 μ m in thickness. This polyamide skin layer typically has internal crosslinking.

In the method of producing a composite reverse osmosis membrane of the present invention, as disclosed in Published Examined Japanese Patent Application No. 63-36803, the obtained composite reverse osmosis membrane can be further chlorinated with hypochlorous acid or the like to improve the salt rejection property.

Examples and Comparative Examples are explained below.

Example 1

A solution A was prepared as an aqueous solution containing 2.0

weight % of m-phenylenediamine, 0.15 weight % of sodium lauryl sulfate, 2.0 weight % of triethylamine, 4.0 weight % of camphorsulfonic acid, and 8 weight % of isopropyl alcohol. The solution A was contacted with a porous polysulfone support film, and extra solution was removed. And thus, a film of the solution A was formed on the support film.

Subsequently, an isooctane solution containing 0.12 weight % of trimesic acid chloride (solution B) was contacted with the support film surface. Before the solution B dried, a solution C, which was an isooctane solution containing 0.5 weight % of trimesic acid chloride was contacted with the layer. The reaction mixture was kept in a 120°C hot air dryer for three minutes in order to form a polyamide skin layer thereon, and thus, a composite reverse osmosis membrane was obtained.

The properties of the composite reverse osmosis membrane was evaluated using pH 6.5 saline water containing 500ppm of sodium chloride. When the operation pressure was 5kgf/cm², the salt rejection was 99.5% and the flux was 1.1m³/m²·day in terms of permeate conductivity.

The obtained composite reverse osmosis membrane was dried for one hour at 60°C. Distilled water was dropped on the film surface (polyamide skin layer surface) and the contact angle was measured 15 seconds later. The contact angle was 39°.

Examples 2, 3 and Comparative Examples 1, 2

Composite reverse osmosis membranes were obtained in the same manner as Example 1 except that the concentration of the trimesic acid chloride in the solution C was varied. Properties of these membranes were evaluated in the same manner as Example 1. The results are shown in the following Table 1.

Example 4

A composite reverse osmosis membrane was obtained in the same manner as Example 1 except that the support film was contacted with the solution C after the solution B was dried visually. Properties of the membrane were evaluated in the same manner as Example 1. The results are shown in the following Table 1.

Table 1

	*I (wt%)	Salt rejection (%)	Flux (m ³ /m ² ·day)	Water contact angle (°)
Example 2	0.25	99.5	0.9	29
Example 3	1.0	99.5	1.0	32
Example 4	0.50	99.5	0.8	39
Com. Ex. 1	0.00	93	0.7	51
Com. Ex. 2	0.12	97	0.7	47

*I: concentration of polyfunctional acid halide compound in solution C

5

As described above, for the composite reverse osmosis membranes of the present invention, the water contact angle is 45° or less, and the concentration of the trimesic acid chloride in the solution C is higher (at least 1.2 times) than that of the solution B. As shown in Table 1, the composite reverse osmosis membranes in the Examples have a high flux and a high salt rejection, so they are excellent composite reverse osmosis membranes. These properties are highest for the membranes in the Examples 1, 2 and 3, where the solution C was contacted while the solution B was not dried yet.

On the other hand, the composite reverse osmosis membranes of the Comparative Examples have water contact angles over 45°, and the flux was low.

INDUSTRIAL APPLICABILITY

As mentioned above, composite reverse osmosis membranes of the present invention have salt rejection and water permeability properties exceeding required levels. By using the composite reverse osmosis membrane, components such as salts can be sufficiently separated even at a low operation pressure. Because of the low pressures, water purification equipment can be composed of pipes made of inexpensive materials such as polyvinyl chloride, providing a cost reduction. Moreover, the composite reverse osmosis membrane of the present invention can be used for a domestic water purification apparatus since it can be operated at city water level pressures.

CLAIMS

1. (Amended) A composite reverse osmosis membrane comprising:
a porous support; and
a polyamide skin layer formed on the porous support,
wherein the contact angle between the polyamide skin layer surface and water is no more than 45° , the salt rejection is at least 98%, and the permeate flow rate is at least $0.5 \text{ m}^3/\text{m}^2 \cdot \text{day}$ when evaluated by using feed water which has pH 6.5, 0.05 weight % of salt, an operation pressure of 5 kgf/cm^2 and a temperature of 25°C .
2. The composite reverse osmosis membrane according to claim 1, wherein the contact angle is no more than 40° .
3. The composite reverse osmosis membrane according to claim 1, wherein the polyamide skin layer is formed by reacting a compound having at least two reactive amino groups and a polyfunctional acid halide compound having at least two reactive acid halide groups.
4. (Cancelled)
5. The composite reverse osmosis membrane according to claim 1, wherein the salt rejection is at least 98% and the water permeability is at least $0.6 \text{ m}^3/\text{m}^2 \cdot \text{day}$ when evaluated by using feed water which has pH 6.5, 0.05 weight % of salt, an operation pressure of 5 kgf/cm^2 and a temperature of 25°C .
6. A method of producing a composite reverse osmosis membrane comprising the steps of:
forming a layer by coating on a porous support a solution A comprising a compound having at least two reactive amino groups;
contacting the layer with a solution B comprising a polyfunctional acid halide compound; and
subsequently contacting the layer with a solution C comprising a polyfunctional acid halide compound of a higher concentration than the solution B in order to form a polyamide skin layer.

7. The method according to claim 6, wherein the solution C contains the polyfunctional acid halide compound at least 1.2 times in concentration of the solution B.

8. The method according to claim 6, wherein the solution C contains the polyfunctional acid halide compound ranging from 1.3 to 5000 times in concentration of the solution B.

9. The method according to claim 6, wherein the solution B partially remains unreacted at a contact with the solution C.

10. The method according to claim 6, wherein the compound in the solution A comprises at least two reactive amino groups, and the compound is at least one selected from the group consisting of aromatic polyfunctional amine, aliphatic polyfunctional amine and alicyclic polyfunctional amine.

11. The method according to claim 10, wherein the aromatic polyfunctional amine is at least one selected from the group consisting of m-phenylenediamine, p-phenylenediamine, 1,3,5-triaminobenzene, 1,2,4-triaminobenzene, 3,5-diamino benzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, amidol, and xylenediamine; the aliphatic polyfunctional amine is at least one selected from the group consisting of ethylenediamine, propylenediamine and tris(2-aminoethyl)amine; and the alicyclic polyfunctional amine is at least one selected from the group consisting of 1,3-diaminocyclohexane, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, piperazine, 2,5-dimethylpiperazine and 4-aminomethylpiperazine.

12. The method according to claim 6, wherein the polyfunctional acid halide compound contained in the solution B and solution C is at least one selected from the group consisting of aromatic polyfunctional acid halide compound, aliphatic polyfunctional acid halide compound, and alicyclic polyfunctional acid halide compound.

13. The method according to claim 12, wherein the aromatic polyfunctional acid halide compound is at least one selected from the group consisting of

trimesic acid chloride, terephthalic acid chloride, isophthalic acid chloride, biphenyldicarboxylic acid chloride, naphthalenedicarboxylic acid dichloride, benzene trisulfonic acid chloride, benzene disulfonic acid chloride, and chlorosulfonium benzene dicarboxylic acid chloride;

the aliphatic polyfunctional acid halide compound is at least one selected from the group consisting of propanetricarboxylic acid chloride, butanetricarboxylic acid chloride, pentanetricarboxylic acid chloride, glutaryl halide, and adipoyl halide; and

the alicyclic polyfunctional acid halide compound is at least one selected from the group consisting of cyclopropanetricarboxylic acid chloride, cyclobutanetetracarboxylic acid chloride, cyclopentanetricarboxylic acid chloride, cyclopentanetetracarboxylic acid chloride, cyclohexanetricarboxylic acid chloride, tetrahydrofuran tetracarboxylic acid chloride, cyclopentanedicarboxylic acid chloride, cyclobutanedicarboxylic acid chloride, cyclohexanedicarboxylic acid chloride, and tetrahydrofuran dicarboxylic acid chloride.

14. The method according to claim 6, wherein the polyfunctional acid halide compound contained in at least either the solution B or solution C has a hydrophilic group.

15. The method according to claim 14, wherein the hydrophilic group is at least one selected from the group consisting of $-\text{COOX}$, $-\text{OH}$, $-\text{SO}_3\text{X}$, $-\text{OSO}_3\text{X}$, $-\text{NH}_2$, $-\text{NR}_3\text{Y}$ and $-(\text{OCH}_2\text{CH}_2)-$, where X indicates a hydrogen atom, an alkaline metal or $-\text{NH}_4$, R indicates a hydrogen atom or an alkyl group, and Y indicates a halogen.

16. The method according to claim 6, wherein the porous support is further contacted with at least one aqueous solution, comprising either an acidic aqueous solution or an alkaline aqueous solution after the contact with the solution C.

17. The method according to claim 16, wherein the pH of the acidic aqueous solution ranges from 1 to 5 while the pH of the alkaline aqueous solution ranges from 8 to 13.

ABSTRACT

A composite reverse osmosis membrane is described, which includes a polyamide skin layer on a porous support, with a contact angle between the polyamide skin layer surface and water of 45 ° or less. The composite reverse osmosis membrane has a high salt rejection and also a high water permeability. This composite reverse osmosis membrane is produced by forming a polyamide skin layer on a porous support having the steps of: forming a layer on the porous support by coating a solution A including one or more compounds having at least two reactive amino groups; contacting the layer with a solution B comprising one or more polyfunctional acid halide compounds; and subsequently, contacting the layer with a solution C comprising the polyfunctional acid halide compound of a higher concentration than the solution B. The concentration of the polyfunctional acid halide compound in the solution C is preferably at least 1.2 times of the solution B.

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。
私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

上記発明の明細書（下記の欄で×印が付いていない場合は、本書に添付）は、

☐ 年 月 日に提出され、米国出願番号または特許協定条約国際出願番号を _____ とし、
（該当する場合） _____ 日に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、同内容を理解していることをここに表明します。

私は、第37編連邦規則法典第1章56条に定義される通り、特許資格の有無について重大な意味を持つ情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

COMPOSITE REVERSE OSMOSIS MEMBRANE AND
METHOD OF PRODUCING THE SAME

the specification of which is attached hereto unless the following box is checked:

☒ was filed on 29 June 1998
as United States Application Number or PCT
International Application Number PCT/JP98/02954
and was amended on 26 April 1999 (if applicable).

I hereby state I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

Japanese Language Declaration

日本語宣言書

私は、第35編米国法典119章に基づき下記の外国でなされた特許もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張した出願の前に提出された特許または発明者証の外国出願を以下に示しています。

I hereby claim foreign priority under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

過去の外国における出願

9-176904
(Number)
(番号)

Japan
(Country)
(国名)

2 July 1997
(Day/Month/Year Filed)
(出願年月日)

優先権の主張

☒ ☐
Yes No
はい いいえ

(Number)
(番号)

(Country)
(国名)

(Day/Month/Year Filed)
(出願年月日)

☐ ☐
Yes No
はい いいえ

(Number)
(番号)

(Country)
(国名)

(Day/Month/Year Filed)
(出願年月日)

☐ ☐
Yes No
はい いいえ

私は、第35編米国法典120章に基づいて下記の米国特許出願に授与された利益をここに主張します。また、本出願の各請求範囲の内容が過去に第35編米国法典112章第1条で規定された方法で米国特許出願により開示されていない限り、過去の米国出願書提出日以降、本出願書の日本国内または特許協力条約国際提出日までの期間中に入手され、しかも第37編連邦規則法典1章56条で定義された特許資格の有無に重大な意味のある情報については、開示義務があることを私は認めます。

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application

(Application Serial No.)
(出願番号)

(Filing Date)
(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済み、係属中、放棄済み)

(Application Serial No.)
(出願番号)

(Filing Date)
(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済み、係属中、放棄済み)

私は本書中の私自身の知識に基づき表明が真実であり、かつ他から聞いた情報及び私が信じることを基とする表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びその他は第18編米国法典第1001章に基づき罰金、または拘禁、もしくはその両方により罰せられること、またそのような故意の虚偽による表明があると出願または許可された特許の有効性が損なわれることを承知の上で上記表明をなしていることをここに宣言致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief and believed to be true; and further that these statements were made with the knowledge that willful false statements and like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration

日本語宣言書

委任状: 下記の発明者として、私は本出願の手続きを遂行し、同出願に関連する特許商標庁との一切の取引を取り扱うため、以下の弁護士及び(または)代理人をここに指名致します。(弁護士、代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (*list name and registration number*)

Jonathan P. Osha, Reg. No. 33,986
 Alan D. Rosenthal, Reg. No. 27,833
 Richard A. Fagin, Reg. No. 39,182
 K. KaRan Reed, Reg. No. P45,036
 David E. Mixon, Reg. No. 43,809
 Adenike Adewuya, Reg. No. 42,254
 Daniel G. Nguyen, Reg. No. 42,933
 Thomas K. Scherer, Reg. No. 45,079

書類送付先

Send Correspondence to:

Jonathan P. Osha
ROSENTHAL & OSHA L.L.P.
700 Louisiana Street, Suite 4550
Houston, Texas 77002

電話による直接連絡先: (名前及び電話番号)

Direct Telephone Calls to: (*name and telephone number*)

Jonathan P. Osha
 (713)228-8600

唯一または第一発明者

Full name of sole or first inventor

Masahiko HIROSE

発明者の署名

日付

Inventor's signature

date

Masahiko Hirose November 17, 1999

住所

Residence

203-11, Ryousenji, Ritto-cho, Kurita-gun, Shiga 520-3035, JAPAN

国籍

Citizenship

Japan

私書箱

Post Office Address

203-11, Ryousenji, Ritto-cho, Kurita-gun, Shiga 520-3035, JAPAN

第二共同発明者 (該当する場合)

Full name of second joint inventor, if any

Hiroki ITO

第二発明者の署名

日付

Second inventor's signature

date

Hiroki Ito November 17, 1999

住所

Residence

8-31, Shibukawa 2-chome, Kusatsu-shi, Shiga 525-0026 JAPAN

国籍

Citizenship

Japan

私書箱

Post Office Address

8-31, Shibukawa 2-chome, Kusatsu-shi, Shiga 525-0026 JAPAN

(第三以降の共同発明者についても同様の情報及び署名を記載のこと)

(Supply similar information and signature for third and subsequent joint inventors)

第三発明者	20	Full name of third inventor Tomomi OHARA
同第三発明者の署名	日付	Third Inventor's signature Tomomi Ohara date November 17, 1999
住所		Residence 3-8, Oji 2-chome, Kusatsu-shi, Shiga 525-0032 JAPAN
国籍		Citizenship Japan
私書箱		Post Office Address 3-8, Oji 2-chome, Kusatsu-shi, Shiga 525-0032 JAPAN